Electronic supplementary information (ESI)

Cyclic CO_2 absorption/desorption property of Li_3NaSiO_4 under the partial pressure of CO_2 for practical applications

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XRD measurements of prepared Li_3NaSiO_4 were performed right before the other characterizations. Because the small peaks assigned as Li_2SiO_3 were observed in addition to the main peaks identified as Li_3NaSiO_4, Rietveld analysis was conducted assuming the coexistence of the two phases. Fig. S1 shows the results of the Rietveld analysis of the X-ray diffraction (XRD) patterns of Li_3NaSiO_4 used in this study. The Bragg angles of Li_3NaSiO_4 and Li_2SiO_3 are represented by green and pink bars, respectively. The blue curve represents the difference in the experimentally obtained data (●) and calculated data (red curve). The obtained parameters are listed in Tab. S1.

The calculated weight ratio of Li_3NaSiO_4/Li_2SiO_3 was 0.9842/0.0158. The purity of Li_3NaSiO_4, calculated by assuming that the same molar of $LiNaCO_3$ with Li_2SiO_3 was present owing to an incomplete reaction, was 96.9 wt%.

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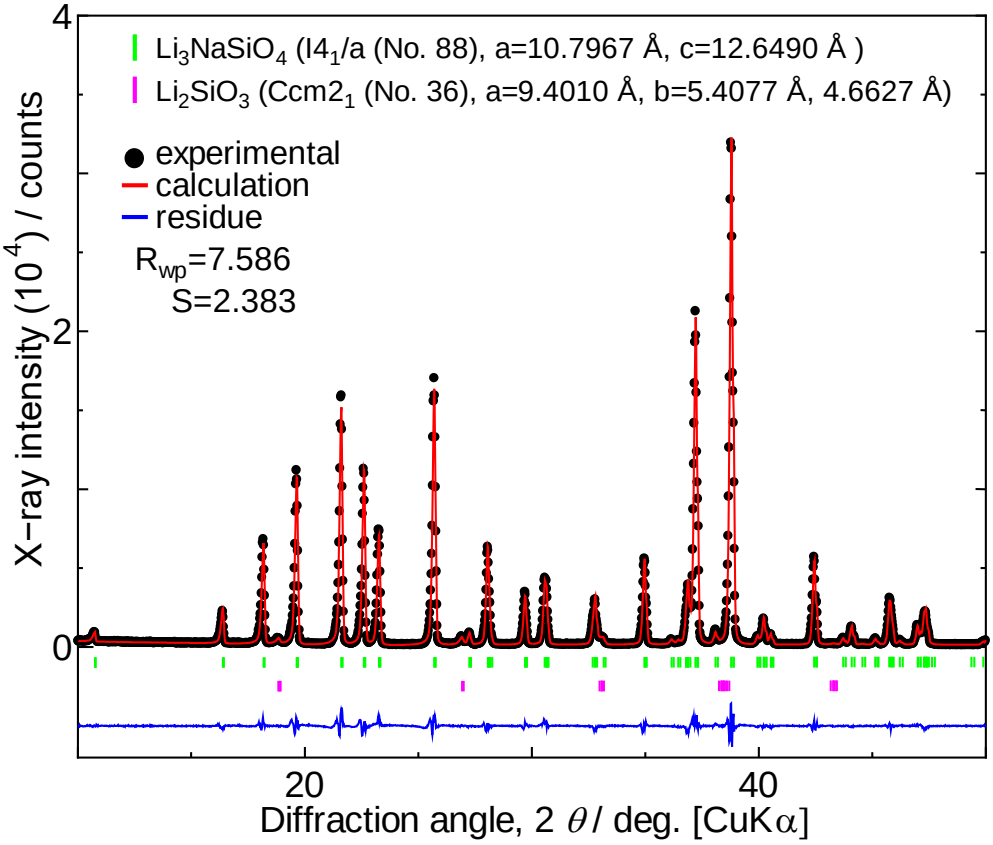

Fig. S1 Results of the Rietveld analysis of X-ray diffraction pattern of Li_3NaSiO_4 used in this study.

Tab. S1 Parameters obtained from the Rietveld analysis.

phase	**atom**	**Wyckoff position**	**occupancy**	**x**	**y**	**z**	**B**
Li_3NaSiO_4	Si	16 f	1.0	0.4626	0.06681	0.1945	1.159
	Na	16 f	1.0	0.2791	0.01566	0.5952	1.500*
	Li1	16 f	1.0	0.1579	0.7198	0.8159	0.3161
	Li2	16 f	1.0	0.1624	0.2355	0.6933	0.4097
	Li3	16 f	1.0	0.1322	-0.2511	0.5696	0.1000*
	O1	16 f	1.0	0.4516	-0.07604	0.7021	0.5000*
	O2	16 f	1.0	0.3516	0.2126	0.6649	0.5000*
	O3	16 f	1.0	0.1611	-0.1546	0.7042	0.5360
	O4	16 f	1.0	0.9172	0.4212	0.6831	0.5000*
Li_2SiO_3	Si	4 a	1.0	0.0000	0.1823	0.4416	0.1200
	Li	8 b	1.0	0.1718	0.3505	-0.08323	0.1000*
	O1	8 b	1.0	0.1607	0.3070	0.4132	0.5348
	O2	4 a	1.0	0.0000	0.1237	0.8549	1.000*

* fixed for convergence

Fig. 1(a) in the main text is enlarged as Fig. S2 to clearly distinguish the reaction at the starting temperature. The temperature dependence of the reaction ratio of the Li_2SiO_3/Li_2CO_3 mixture under various $P(CO_2)$ values calculated from TG (black curves) and the differential of TG (DTG: red curves) are shown in Fig. S2. Further, the temperatures at which DTG curves deviate from 0.00, represented by arrows, are considered as reaction starting temperatures.

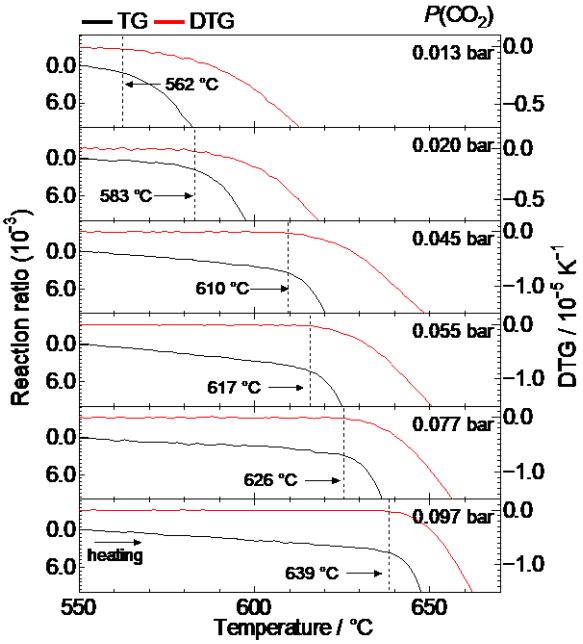

Fig. S2 Enlargement of Fig. 1(a). Temperature dependence of the reaction ratio of Li_2SiO_3/Li_2CO_3 mixture under various $P(CO_2)$ values calculated from TG (black curves) and differential of TG (DTG: red curves).

Fig. S3 shows the XRD pattern of CO_2-absorbed Li_3NaSiO_4 specimen at 650 °C under CO_2/N_2 mixed gas with $P(CO_2)$ of 0.10 bar after successive cooling under the same CO_2/N_2 mixed gas. The XRD pattern indicated that the specimen was a mixture of Li_2SiO_3 and $LiNaCO_3$, indicating that reaction (2) occurred during the heat treatment.

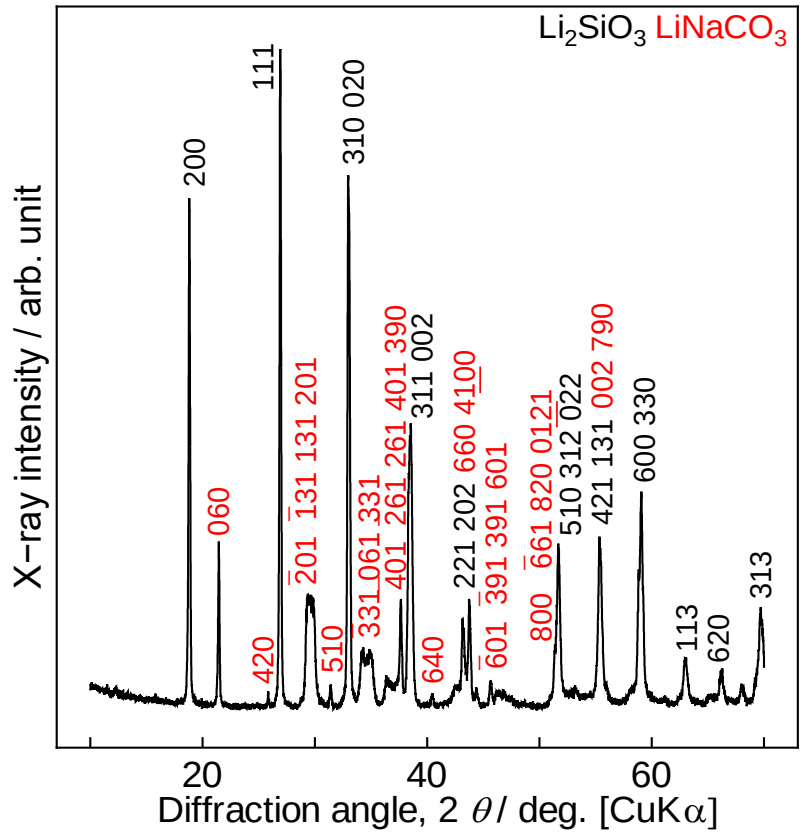

Fig. S3 XRD pattern of CO_2 absorbed Li_3NaSiO_4 specimen at 650 °C under CO_2/N_2 mixed gas with $P(CO_2)$ of 0.10 bar after successive cooling. The black and red Miller index represent peaks identified as Li_2SiO_3 (JCPDS No. 29-0829) and $LiNaCO_3$ (JCPDS No. 34-1193), respectively.

Fig. S4 shows SEM images of Li_2SiO_3 prepared by (a) 1st and (b) 5th CO_2 absorption at 650 ºC in Fig. 4 and successive cooling in the CO_2/N_2 mixed gas with $P(CO_2)$ of 0.10 bar. Cogenerated $LiNaCO_3$ was removed by the treatment of dilute HNO_3. Needle-like crystals with shorter edges of ~2 μm were observed in (a). Although an increase in size was observed, a large increase in size was not observed in (b).

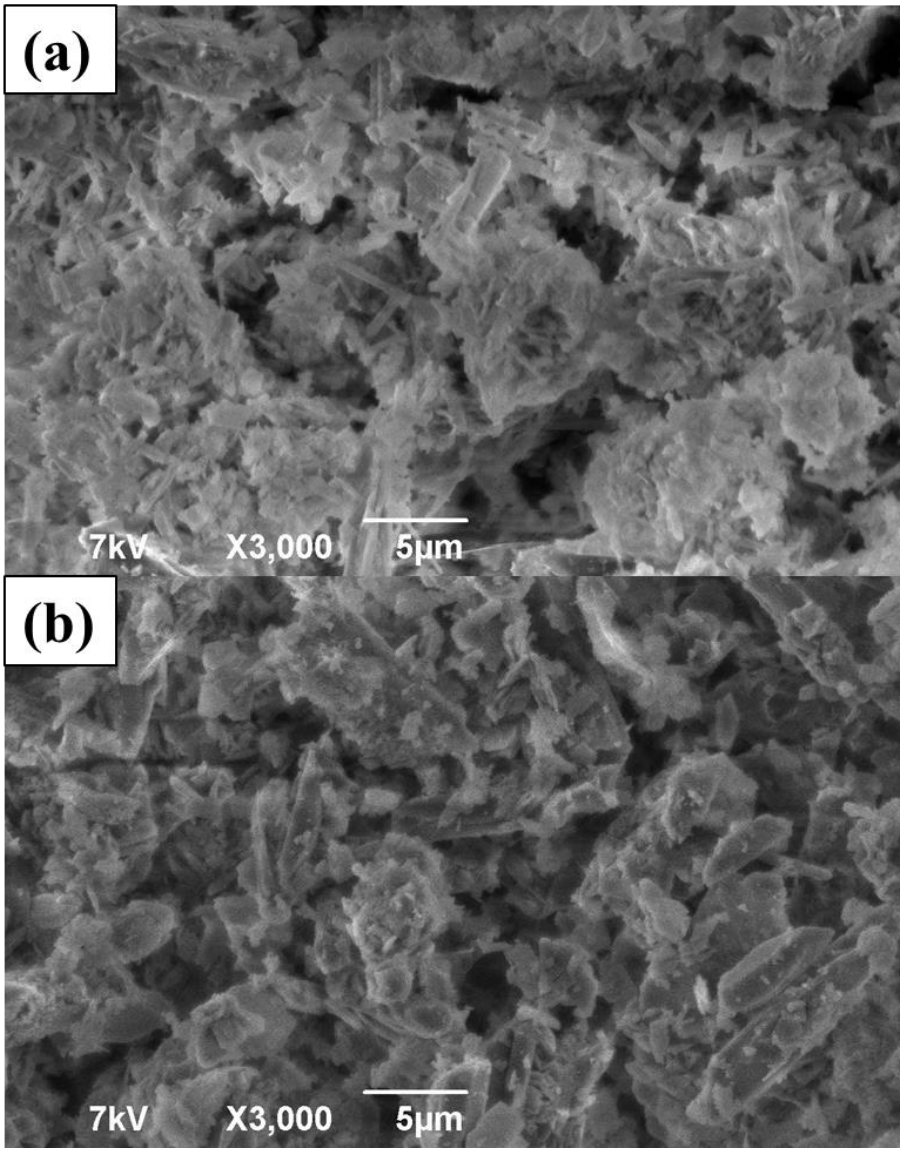

Fig. S4 SEM images of Li_2SiO_3 prepared by (a) 1st and (b) 5th CO_2 absorption at 650 ºC in Fig. 4 and successive cooling in the CO_2/N_2 mixed gas with $P(CO_2)$ of 0.10 bar. Cogenerated $LiNaCO_3$ was removed by immersing in dilute HNO_3.